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# Synthesis, spectral studies and quantum-chemical investigations on S-benzyl $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate



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## KEYWORDS

Semi-empirical methods;  
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PM3;  
Vibration modes;  
Correlation coefficient;  
Hardness ( $\eta$ )

**Abstract** A new Schiff base of S-benzylthiocarbazate has been synthesized by the 1:1 condensation of 4-NN biscynodiethylaminobenzaldehyde and S-benzylthiocarbazate. The structure of Schiff base was determined by FT-IR and <sup>1</sup>H NMR spectroscopic data. The synthesized Schiff base molecule has been subjected to theoretical studies by using semi-empirical AM1 and PM3 quantum-chemical methods. The molecular geometry, vibration frequencies, HOMO–LUMO energy gap, molecular hardness ( $\eta$ ), ionization energy (IE), electron affinity (EA), total energy and dipole moment were analyzed. The experimental results of the compound have been compared with theoretical results and it is found that the experimental data show good agreement with calculated values.

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## 1. Introduction

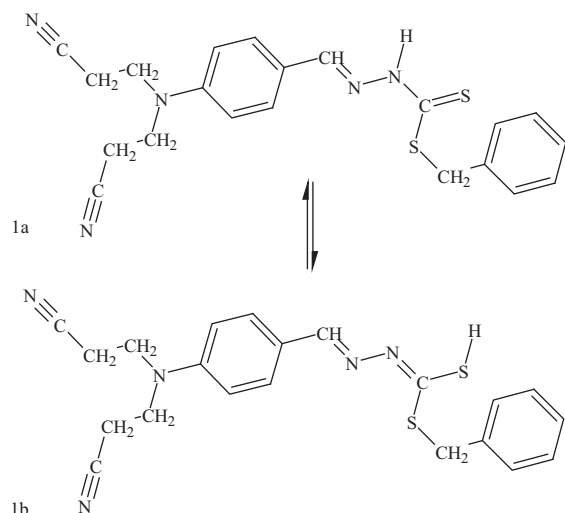
S-alkyl/aryl dithiocarbazate and its Schiff bases have been extensively studied over last decade (Ray et al., 2007; Ali et al., 2008; Singh et al., 2010). The attention on these

compounds arose mainly due to their potential biological activities (Hossian et al., 1993; Morya et al., 2003; Pavan Fernando et al., 2008). However, no theoretical study on this Schiff base has been reported in the literature so far. Now, the computational chemistry becomes an indispensable tool for theoretical studies of molecules in organic chemistry and related fields (Rogers, 2003; Jensen, 2007; Bouklah et al., 2012; Kumar et al., 2013; Serda et al., 2013). Recently Patil and co-workers have studied the synthesis, photo-physical and DFT studies of ESIPT inspired novel 2-(2',4'-dihydroxyphenyl) benzimidazole, benzoxazole and benzothiazole. They have showed absorption–emission characteristic for the molecules as a function of pH and reported good agreement

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**Figure 1** Tautomeric forms of the S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate (1a; thione form and 1b; thiol form).

between theoretical and experimental results (Patil et al., 2013). El-Sheshtawy and Abou Baker have also compared experimental photophysical properties with the computed values (El-Sheshtawy et al., 2014).

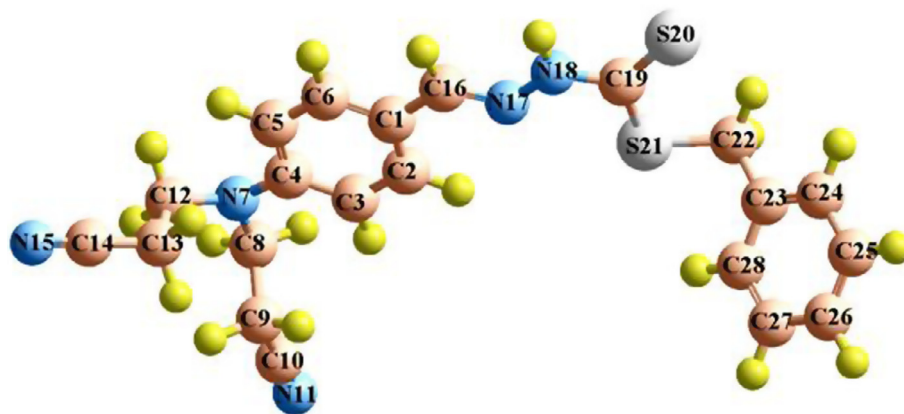
Semi-empirical computational methods have been widely applied for theoretical investigations of various organic molecules (Hameed, 2005, 2006; Matos et al., 2013; Cojocaru et al., 2013; Arora et al., 2011; Singh et al., 2012, 2013). These methods use a simpler Hamiltonian than the correct molecular Hamiltonian and are based on parameters whose values are adjusted to fit experimental data. Semi-empirical methods are advantageous over *ab initio* methods for study of medium and large molecules as these methods in general do not make use of symmetry in SCF cycles in economizing the CPU time.

Several semi-empirical two-electron MO generalizations were developed that are applicable to both planer and non-planer molecules. The CNDO (Complete Neglect of Differential Overlap) and INDO (Intermediate Neglect of Differential Overlap) methods treat only the valence electrons precisely. (Pople et al., 1967). The NDDO (Neglect of Diatomic Differential Overlap) is an improvement on INDO in which differential overlap is neglected only between atomic orbitals centered on different atoms (Pople and Segal, 1965). Dewar

**Table 1** Calculated bond lengths and bond angles of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate Schiff base by AM1 and PM3 semi-empirical methods.

	Bond lengths (Å)				Bond angles (°)		
	Exp.	AM1	PM3		Exp.	AM1	PM3
C1—C2	1.388	1.39972	1.39857	C1—C2—C3	121.9	120.918	120.401
C2—C3	1.367	1.38963	1.3875	C2—C3—C4	121.3	121.092	120.532
C3—C4	1.402	1.41549	1.40245	C3—C4—C5	116.8	117.422	118.952
C4—C5	1.377	1.41887	1.40559	C4—C5—C6	120.9	120.852	120.304
C5—C6	1.374	1.38692	1.38415	C2—C1—C6	—	118.492	119.148
C1—C6	1.440	1.40290	1.40082	C3—C4—N7	121.3	121.900	120.863
C4—N7	1.443	1.40557	1.43884	C4—N7—C8	120.3	119.816	118.246
N7—C8	1.388	1.44101	1.48142	N7—C8—C9	—	116.217	115.802
N7—C12	1.367	1.44287	1.48222	C8—C9—C10	—	110.287	110.343
C8—C9	—	1.53779	1.53292	C9—C10—N11	—	179.514	179.661
C9—C10	—	1.44427	1.44657	C5—C4—N7	121.9	120.569	119.955
C10—N11	—	1.16287	1.15885	C4—N7—C12	—	119.289	117.544
C12—C13	—	1.53784	1.5332	N7—C12—C13	—	115.747	115.373
C13—C14	—	1.44150	1.44634	C12—C13—C14	—	110.296	110.388
C14—N15	—	1.62920	1.15887	C13—C14—N15	—	179.504	179.726
C1—C16	—	1.46266	1.46169	C2—C1—C16	—	122.970	122.592
C16—N17	1.274	1.38780	1.30257	C6—C1—C16	—	118.530	118.258
N18—C19	1.324	1.39129	1.40202	C16—N17—N18	114.0	121.017	120.963
C19—S20	1.611	1.59219	1.63593	N17—N18—C19	122.4	122.378	120.050
C19—S21	1.742	1.71605	1.76977	N18—C19—S20	120.5	119.251	118.199
S21—C22	1.817	1.77184	1.83194	N18—C19—S21	114.6	115.401	116.247
C22—C23	1.498	1.47839	1.48631	S20—C19—S21	124.0	125.348	125.535
C23—C24	1.373	1.40083	1.39728	C19—S21—C22	102.4	104.103	104.747
C24—C25	1.405	1.39398	1.38993	S21—C22—C23	107.6	112.403	113.334
C25—C26	1.344	1.39446	1.39112	C22—C23—C24	122.2	120.141	119.970
C26—C27	1.328	1.39522	1.39106	C23—C24—C25	120.0	120.166	119.964
C27—C28	1.368	1.39308	1.38975	C24—C25—C26	120.0	120.197	120.206
C23—C28	1.360	1.40134	1.39690	C25—C26—C27	120.6	119.865	119.943
—	—	—	—	C26—C27—C28	119.8	120.144	120.031
—	—	—	—	C27—C28—C23	122.8	120.231	120.031
—	—	—	—	C24—C23—C28	—	119.396	119.699
Correlation coefficient (cc)		<b>0.951</b>	<b>0.962</b>			<b>0.920</b>	<b>0.920</b>

Validation between experimental and theoretical results has been given in terms of correlation coefficients (cc).



**Figure 2** Optimized molecular structure of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate.

and co-workers devised several semi-empirical SCF MO theories that closely resemble the INDO and NDDO methods. Austin Model 1 (AM1) an improved version of MNDO has been parameterized for H, B, Al, C, Si, Ge, Sn, N, P, O, S, Cl, I, Zn, and Hg atoms (Dewar and Thiel, 1985; Dewar and Yuan, 1990). AM1 is re-parameterized to give the PM3 method (Parametric method 3). PM3 has been parameterized for H, C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, F, Cl, Br, Al, Ga, In, Tl, Be, Mg, Zn, Cd and Hg atoms. Semi-empirical methods are widely available in many programs/packages like MOPAC, Gaussian, Hyperchem, Chemoffice, etc.

In this study, we report the synthesis and characterization of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate and theoretical investigations like, molecular geometry, vibrational spectra, HOMO–LUMO energy gap, molecular hardness ( $\eta$ ), ionization energy (IE), electron affinity (EA), total energy and dipole moment.

## 2. Experimental

All the chemicals and solvents were of analytical grade and were used as received. The FT-IR spectrum in KBr pellets ( $500\text{--}4000\text{ cm}^{-1}$ ) was recorded using an FT-IR spectrophotometer Shimadzu 8201 PC Perkin. The  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  was recorded on Bruker DRX-300 FT NMR. All these measurements were done at Sophisticated Analytical Instrument Facility (SAIF), CDRI, Lucknow, India.

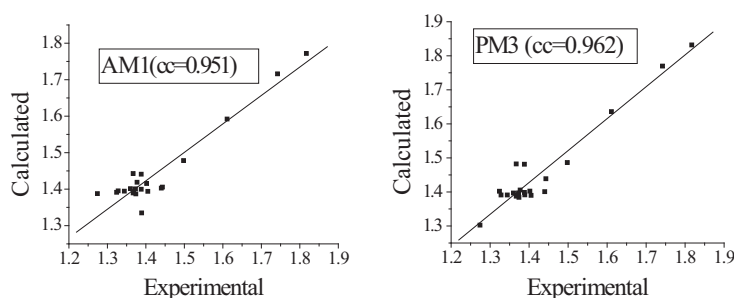
S-benzyl dithiocarbazate was prepared as described in the literature (Tarafedr et al., 2000).

### 2.1. Synthesis of S-benzyl $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate

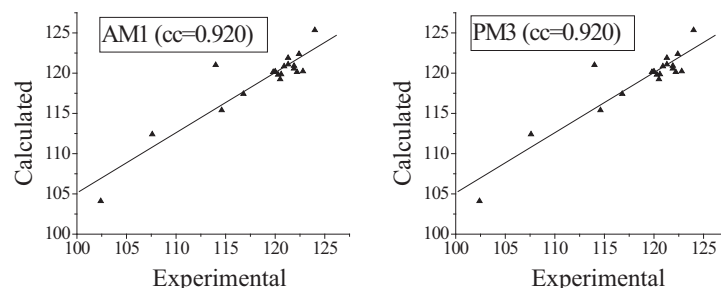
A solution of SBDTC (1.98 g, 0.1 mol) in absolute ethanol (40 ml) was added to an equimolar solution of 4-NNbiscynodiethylaminobenzaldehyde in 50 ml of the same solvent. The mixture was heated on a steam bath for 10 min. and then cooled to  $0^\circ\text{C}$  in an ice bath. Precipitated Schiff base was filtered, washed with cold ethanol and dried in vacuum over silica gel. Yield: 52%. Melting point  $176^\circ\text{C}$ , FT-IR (KBr),  $\nu\text{ cm}^{-1}$ : 3105.2 m, 2970.2 m (N–H), 1593.1 s (C=N), 1508.2 m (C=C), 1353.9 s (C–N), 1315 m, , 1184.2 m, 1091.6 m (N–N), 1026.1 s (C=S), 810.0 m (N–C–S), 709.8 w, 644.2 w, 624.9 w,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.2 (s, 1H), 2.6 (t, 4H), 3.8 (t, 4H), 4.5 (s, 2H), 6.6–8.0 (m, 9H). Elemental analysis: Calculated for  $\text{C}_{21}\text{H}_{21}\text{N}_5\text{S}_2$ : C, 61.90; H, 5.16; N, 17.15%. Found: C, 61.85; H, 5.20; N, 17.15%.

### 2.2. Computational details

Intel based Pentium IV, 630, HT3.2 machine having 800 FSB, 1 GB RAM, 7200 rpm HDD was used to run all the calculations. Semi-empirical AM1 and PM3 quantum chemical calculations were carried out by the HyperChem™ 8.0 Molecular Modeling program (Stewart et al., 1990) with root mean



**Figure 3** Graphical correlations between the experimental and calculated bond lengths of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by semi-empirical AM1 and PM3 methods (cc = correlation coefficient).



**Figure 4** Graphical correlations between the experimental and calculated bond angles of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by semi-empirical AM1 and PM3 methods (cc = correlation coefficient).

**Table 2** Experimental and calculated IR fundamental vibration modes for S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate Schiff base obtained by AM1 and PM3 semi-empirical methods.

Experimental	AM1	PM3
528.5	562.8	536.8
563.2	599.4	561.1
624.9	626.9	589.5
644.2	653.5	614.1
709.8	735.7	760.6
763.8	811.4	799.0
810.0	967.5	840.0
844.8	882.7	858.9
914.2	961.9	952.9
986.2	1003.7	989.8
1002.9	1043.4	996.7
1026.1	1086.7	1027.1
1091.6	1100.8	1034.5
1184.2	1172.7	1086.2
1215.1	1202.7	1151.2
1242.1	1256.6	1163.6
1315.9	1341.8	1233.4
1353.9	1366.1	1275.0
1419.5	1406.8	1343.7
1454.2	1477.9	1403.6
1508.2	1518.3	1464.1
1554.5	1775.8	1516.3
1593.1	1624.7	1536.2
1685.7	1696.7	1638.3
1747.4	1782.4	1782.8
2850.6	2073.4	2802.4
2970.2	3004.6	2805.5
3105.2	3191.5	3029.8
Correlation coefficient (cc)	<b>0.972</b>	<b>0.998</b>
Validation between experimental and theoretical results has been given in terms of correlation coefficients (cc).		

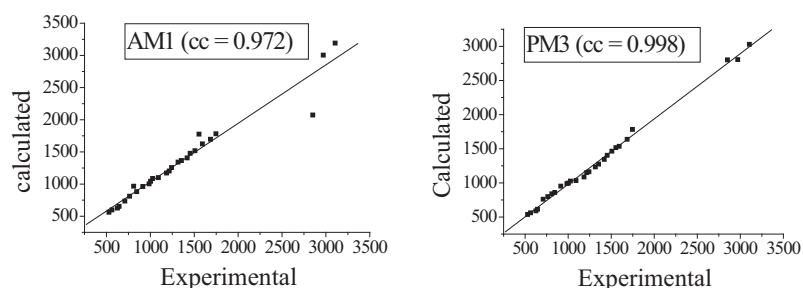
square (RMS) gradient 0.1 kcal/mol using Polak–Ribiere algorithm. All the parameters were allowed to relax and all the calculation converged to an optimized geometry, which corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming that the molecule belongs to  $C_1$  point group symmetry.

### 3. Results and discussion

The S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate has a thione group (C=S) and a proton adjacent to the thione group. It has been stated that the thione group (C=S) is relatively unstable in monomeric form and tends to form a more stable C—S single bond by enethiolization, if there is at least one hydrogen atom adjacent to the thione (C=S) bond (Mayer, 1967). The IR spectrum of the S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate does not display  $\nu(\text{S—H})$  at *ca.* 2570  $\text{cm}^{-1}$ , but  $\nu(\text{N—H})$  modes are present at *ca.* 3105 and 2970  $\text{cm}^{-1}$ , indicating that the thione form predominates in the solid state. The  $^1\text{H}$  NMR spectrum of the Schiff base in  $\text{CDCl}_3$  exhibits the —SH proton signal at 1.2 ppm. No signal, not even a weak one at  $\sim 13.0$  ppm, attributable to —NH proton, is observed in the  $^1\text{H}$  NMR spectrum of the Schiff base, indicating that in solution it exists as a thiol tautomeric form (Fig. 1).

#### 3.1. Optimized structure

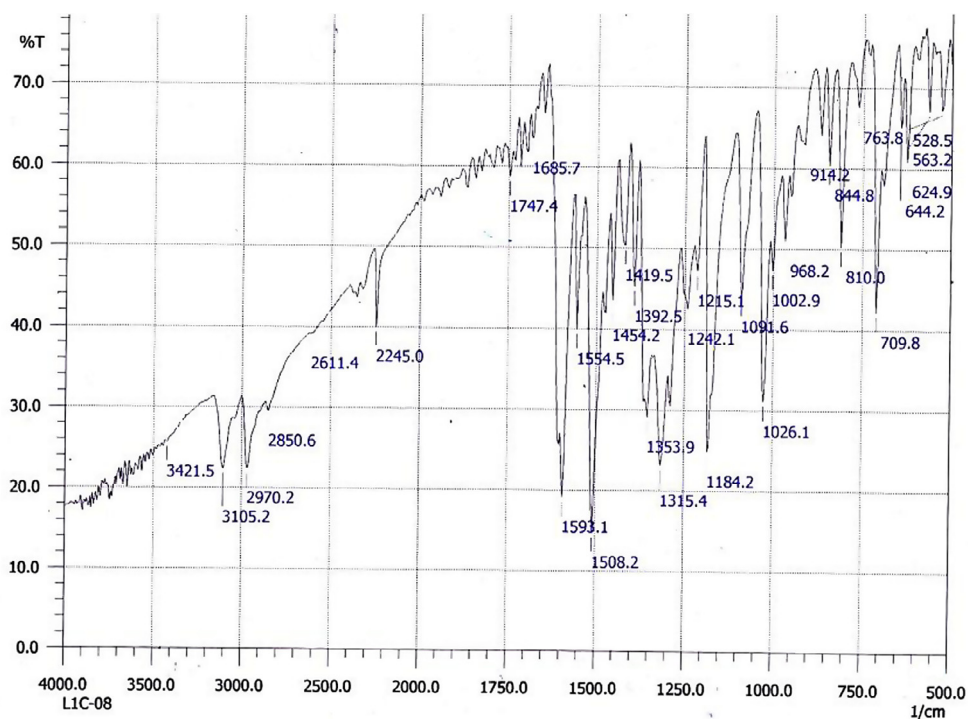
Since the molecular parameters are controlled by the molecular geometry, the crucial step for the calculation of IR spectra is the geometry optimization of the molecule. The optimized structural parameters such as bond length and bond angle of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate calculated by semi-empirical AM1 and PM3 methods are presented in Table 1 in accordance with atom numbering schemes given in Fig. 2. The crystal structure of the exact title Schiff base is not available till now, the optimized structure can only be compared with similar Schiff base of dithiocarbazate for which crystal structure has been solved along with complete optimized bond lengths and bond angles (Fun et al., 1995). Some experimental results of the similar Schiff base are also included in Table 1 for comparison. Optimized structure yields fairly accurate bond length pairs for the bonds C1—C2, C2—C3, C3—C4, C5—C6, C1—C6, C2—N7, N17—N18, N18—C19, C19—S20, C19—S21, S21—C22, C22—C23, C23—C24, C24—C25, C26—C27, C27—C28 and C23—C28 at semi-empirical level of calculations. The values of bond lengths N7—C8, N7—C12, and C16—N17 are greater than experimental values. The increases in bond lengths are due to the presence of bulky groups on N7. The entire bond angles except C16—N17—N18 and S21—C22—C23 deviated by  $< 2^\circ$  compared to experimental data computed at AM1 and PM3 semi-empirical methods which disclosed that both



**Figure 5** Graphical correlations between the experimental and calculated vibration frequencies of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by AM1 and PM3 semi-empirical methods (cc = correlation coefficient).

**Table 3** Experimental and calculated IR spectral frequencies of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate Schiff base obtained by AM1 and PM3 semi-empirical methods with their assignments.

Experimental ( $\nu$ in $\text{cm}^{-1}$ )	Calculated in ( $\nu$ in $\text{cm}^{-1}$ )		Assignments
	AM1	PM3	
3105.2 m	3191.5	3029.8	$\nu(\text{N-H})$ stretching vibration
2970.2 m	3004.6	2805.5	
1593.1 s	1624.7	1536.2	$\nu(\text{C=N})$ coupled with N-H in plane and $\nu(\text{C=C})$ aromatic ring
1508.2 m	1518.3	1464.1	
1353.9 s	1366.1	1275	$\nu(\text{C-N})$ stretching vibration/C-H bending of p-ethylamino substituent
1315 m	1341.8	1233.4	
1184.2 m	1172.7	1086.2	N-H out of plane
1091.6 m	1100.8	1034.5	$\nu(\text{N-N})$ stretching vibration
1026.1 s	1086.7	1027.1	$\nu(\text{C=S})$ stretching vibration
810.0 m	867.5	840.0	$\nu(\text{N-C-S})$ stretching vibration
709.8 w	735.7	760.6	Out of plane ring deformation mode
644.2 w	653.5	614.1	Out of plane bending of ring
624.9 w	626.9	589.5	



**Figure 6** Scan copy of the experimental IR spectrum of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate.



**Table 4** Comparison of HOMO–LUMO energy, hardness ( $\eta$ ), ionization energy (IE), electron affinity (EA), total energy and dipole moment of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by semi-empirical AM1 and PM3 methods.

Energies	AM1	PM3
$\epsilon_{\text{HOMO}}$ (eV)	−8.631368	−8.8867369
$\epsilon_{\text{LUMO}}$ (eV)	−1.046407	−1.605004
$\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$ (eV)	7.584898	7.2817329
Hardness( $\eta$ ) = $\frac{1}{2}(\text{HOMO} - \text{LUMO})$	3.792449	3.6408665
IE = $-\epsilon_{\text{HOMO}}$	8.631368	8.8867369
EA = $-\epsilon_{\text{LUMO}}$	1.046407	1.605004
Total energy (au)	−161.619377	−146.6506248
Dipole moment (Debyes)	1.914	2.157

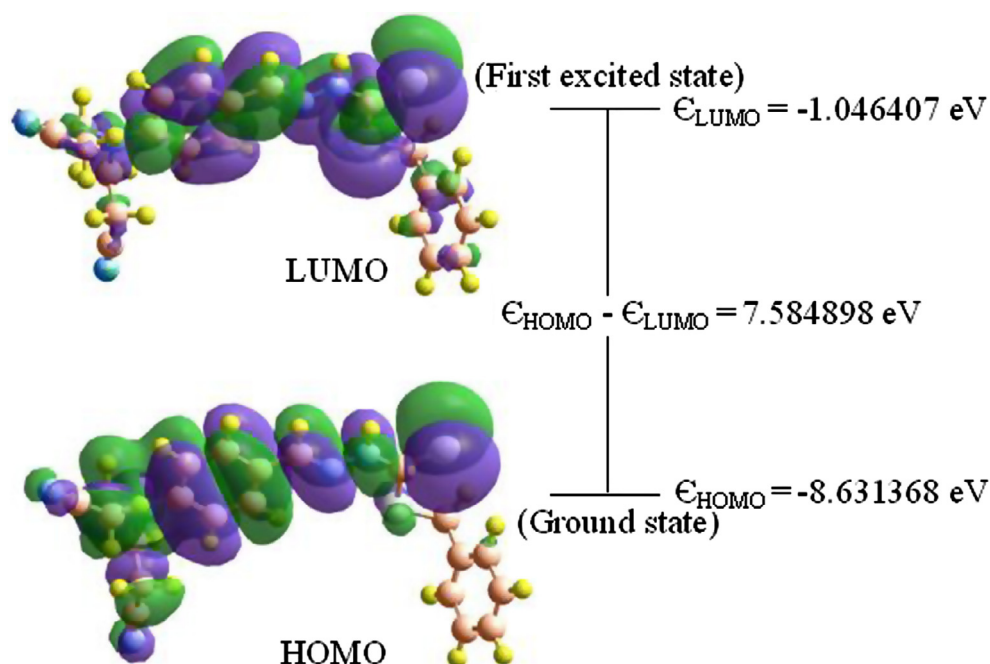
the methods are good to reproduce the bond angles. The most suitable method was found by plotting the experimental values versus calculated values and the obtained correlation coefficients were analyzed (Fig. 3). For bond length, the correlation coefficients obtained for AM1 and PM3 methods were 0.951 and 0.962 respectively. It was evident that PM3 method gave more satisfactory correlation coefficient ( $cc = 0.962$ ) between experimental and calculated bond lengths. In the case of bond angles, both the methods gave same correlation coefficient ( $cc = 0.920$ ). From the theoretical values, it was found that most of the optimized bond angles are slightly larger than the experimental values. It is due to the fact that theoretical calculations of the molecules are performed in gaseous phase and the experimental results of molecules are recorded in solid phase. In spite of the differences, calculated geometric parameters represent a good approximation and they are the basis for calculating other parameters such as vibration frequencies and thermodynamic properties (see Fig. 4).

### 3.2. Vibration frequencies

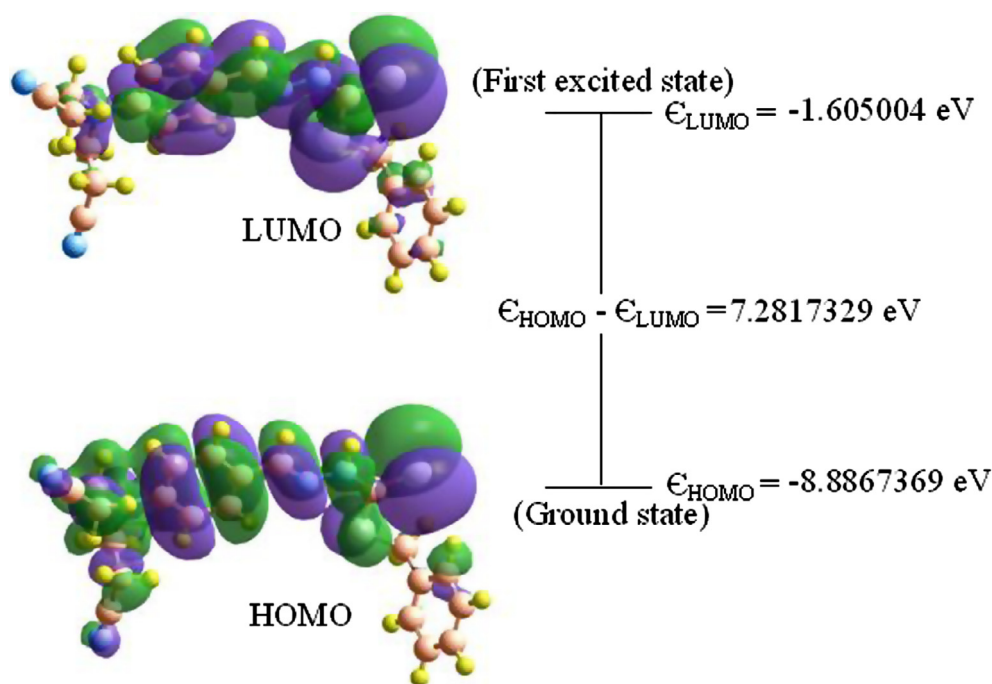
Harmonic vibrational frequencies of the title Schiff base were calculated using the semi-empirical AM1 and PM3 methods. Some observed and calculated frequencies in the infrared spectra of the title Schiff base are shown in Table 2. Because of both symmetry and large size of the system, many vibrations are difficult to describe, in particular those involving the coupled movement of several parts of groups. Some vibrations identified in the solid phase experimental spectra could not be identified in the simulated counterpart and therefore, have been omitted. The differences between calculated and experimental frequencies are due to anharmonicity, intermolecular interaction, an approximation treatment of electron correlation effects and the limited basis sets. To examine the usefulness of the calculation method for IR, a linearity between the experimental and calculated wave numbers has been derived by plotting the calculated versus experimental wave numbers and analyzing correlation coefficient value (Bingham et al., 1975). Graphical correlation between experimental and calculated fundamental vibration frequencies are presented in Fig. 5. The correlation coefficient ( $cc$ ) values obtained for AM1 and PM3 semi-empirical methods are 0.972 and 0.998 respectively. It is evident that PM3 semi-empirical method gives more satisfactory correlation ( $cc = 0.998$ ) between experimental and calculated vibration frequencies. In addition the important IR frequencies with their assignments are shown in Table 3. However, the scan copy of the experimental IR spectrum of S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate Schiff base is also presented in Fig. 6.

### 3.3. Frontier molecular orbital analysis

The frontier orbitals (HOMO and LUMO) of the chemical species are very important in defining its reactivity (Fukui et al.,



**Figure 7** Molecular orbital surface and HOMO–LUMO energy gap for S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by AM1 semi-empirical method.



**Figure 8** Molecular orbital surface and HOMO–LUMO energy gap for S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate obtained by PM3 semi-empirical method.

1952; Mendoza-Huizar and Rios-Reyes, 2011). Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy, empty molecular orbitals. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, hardness ( $\eta$ ), ionization energy (IE), electron affinity (EA), total energy and dipole moment have been calculated and are given in Table 4. Based on AM1 and PM3, optimized geometry, the total energy of the compound has been calculated by these methods, which are  $-161.619377$  and  $-146.6506248$  au respectively. An electronic system with a larger HOMO–LUMO gap should be less reactive than one having smaller gap (Kurtaran et al., 2007). The ionization energy (IE) can be expressed through HOMO orbital energies as  $IE = -\epsilon_{\text{HOMO}}$  and electron affinity (EA) can be expressed through LUMO orbital energies as  $EA = -\epsilon_{\text{LUMO}}$  (Dixon et al., 2003). The hardness ( $\eta$ ) corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO–LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system. In the present study, the HOMO–LUMO gap of the molecule is 7.584898 and 7.2817329 eV for AM1 and PM3 respectively as shown in Table 4, which clearly indicates that the molecule is very stable. The ionization potential values obtained by AM1 and PM3 theoretical methods also support the stability of the title molecule. The calculated dipole moment values show that the molecule is highly polar in nature. 3D plots of the HOMO–LUMO and the corresponding energy levels for the compound obtained by AM1 and PM3 semi-empirical methods are shown in Figs. 7 and 8 respectively.

#### 4. Conclusion

A new Schiff base of S-benzylidithiocarbazate was synthesized. The IR spectrum of the Schiff base indicates that in solid state

it remains in the thione form, where the existence of thiole tautomeric form may be expected in solution. The synthesized Schiff base has been subjected to theoretical studies using AM1 and PM3 semi-empirical calculations on the molecular geometry, atomic charges, dipole moment, vibration frequencies, HOMO–LUMO energy gap, molecular hardness, ionization energy and electron affinity. The correlation coefficients for bond lengths for S-benzyl  $\beta$ -N-(4-NN biscynodiethylaminophenylmethylene)dithiocarbazate Schiff base molecule are 0.951 and 0.962 for AM1 and PM3 methods respectively and PM3 gives more satisfactory correlation. In the case of bond angles, both the methods gave same correlation coefficient ( $cc = 0.920$ ). A good linearity between calculated and experimental vibration frequencies was also observed. Any discrepancy noted between the observed and the calculated frequencies is due to the fact that calculations have been actually done on the single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made with minimal basis set and reasonable deviations from the experimental values seem to be correct. The calculated HOMO–LUMO orbital energies can be used to estimate the ionization energy, molecular hardness and other physical parameters semi quantitatively. HOMO–LUMO energy gap, molecular hardness, ionization energy, electron affinity, total energy and dipole moment are very important physical parameters for chemical reactivity and biological activities of the studied compound.

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